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Research Article

FEASIBILITY STUDY OF USING NATURAL ZEOLITES TO REDUCE SAR IN REVERSE OSMOSIS CONCENTRATE EMPLOYING MANOVA

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ABSTRACT
Nowadays, water and wastewater treatment is one of the most significant worrying problems in various industries. The most important problem industries face is treatment of wastewater output by finding suitable technologies for its disposal so that it does not harm the environment. Various methods are employed to manage wastewater in the utility unit of oil and gas industries in order to treat and reuse the concentrate in irrigation. For this purpose, various parameters in water such as EC must be reduced. In this research on treating reverse osmosis concentrate in the utility unit of Ilam Gas Refinery, two natural types of zeolites (clinopetiolite and metacaoline) were used. This unit produces about 50 m^3 of reverse osmosis concentrate per day, and the possibility of treating this concentrate using natural zeolites was investigated in this research. Moreover, the effects of processing and washing zeolites used in treating the wastewater were studied. To process the used zeolites, they were first washed several times with 0.1M hydrochloric acid and 0.1M caustic soda and then with distilled water. The EC (electrical conductivity) in the reverse osmosis concentrate was in the 1400 to 1600$\mu s/cm$range. Results of the experiments showed the EDTA combination had a negative effect on sodium absorption and on water salinity reduction. Moreover, the processing of zeolites also had a negative effect on sodium absorption and on EC reduction. Results of designing the experiments and of conducting the various tests indicated that both zeolites reduced water salinity but the second type decreased the EC to a greater extent.

Keywords: *Reverse Osmosis Concentrate, Reverse Osmosis, Natural Zeolite, Wastewater*

INTRODUCTION
Reverse osmosis is a membrane technology widely used in water desalinization, production of drinking water, and, recently, more in the third stage of wastewater treatment. This technology enjoys the advantages of membrane processes such as its small size that makes it possible to combine it with other treatment processes. In this technology, semipermeable membranes are used that separate the solution into two flows: pure water that passes through the membrane and the reverse osmosis concentrate (ROC) that contains salts and remaining compounds. The characteristic of the ROC depend on the incoming water, the primary treatment method, and the cleaning procedures. Therefore, concentrations of compounds in the ROC are twice as much or higher compared to those of the incoming water. That is why the disposal method of the ROC influences the designing and implementation of reverse osmosis units (Faghihian *et al.*, 2001).
The ROC of desalinization plants located on the shore is directly disposed of at sea, and recent estimates indicate about 25 million cubic meters of ROC are produced all over the world every day. Roberts *et al.*, (2010) reviewed the ecological effects of desalinization plants and explained that disposal of ROC is a serious potential threat for marine ecosystems, and various studies have shown its unlawful and destructive effects on marine organisms. Moreover, the destructive composition of ROC causes greater destruction, especially in weak ecosystems including those of corals. Furthermore, various chemical factors are added during treatment processes to increase flocculation and prevent the foaming and destruction of the membranes. The mechanism used for reducing the harmful environmental effects of ROC is its dilution with water (Roberts *et al.,* 2010). Other methods that can be used for disposing of ROC from desalinization plants are to inject it into deep wells, discharge it in surface waters, or concentrate it in evaporation ponds. Each of these methods has its own shortcomings and costs of brine disposal are another important point to consider in selecting the desired method.

Gonzalez *et al.*, (2012) presented a review of all treatment and management methods concerning ROC (Faghihian *et al.*, 2001). One of these methods is the use of evaporation ponds, a method that is often used for managing ROC and for its disposal at drinking water production facilities in dry regions. Little mechanical equipment is often required in this method, and it is easy to build and operate the facilities (Mickley, 2001). Use of wind energy in enhancing evaporation has improved this method. Studies have shown that the improved method performs 50 to 90% better than the simple one (Macedonio *et al.*, 2011). Membrane distillation is another method, and research has indicated it can increase recovery from 40 to 89% (Mericq *et al.*, 2010).

Formation of calcium sediments is one of the shortcomings of this method. Grypta studied membrane distillation together with crystallization in 2002 (Gryta, 2002). One of the deficiencies of this method is that it lacks commercial viability. In another study, Ji *et al.*, used lime and soda to recover the ions dissolved in the concentrate by about 34%, which increased the efficiency of reverse osmosis to more than 90% (Ji *et al.*, 2010). Secondary reverse osmosis, alone or together with electrodialysis or together with ion exchange resins, has also been used to treat or reduce the volume of ROC (Acevedo *et al.*, 2010; Al-Wazzan *et al.*, 2003; Ning *et al.*, 2006). Mohammad *et al.*, studied a new project of reducing hardness by two reverse osmosis processes followed by the evaporation-crystallization stage (Mohammadesmaeili *et al.*, 2010a; Mohammadesmaeili *et al.*, 2010b). In another study that Al-Rawafeh *et al.*, (2011) conducted, a combination of three zeolites was used for the pre-treatment of the water fed into reverse osmosis and concluded these compounds had high potential in absorbing substances in seawater (Aiman *et al.*, 2011).

Zeolites are hydrated alkaline and non-alkaline aluminum silicates that can be used as adsorbents, in ion exchange, and as molecular sieves, because of their special structure. Various research has shown natural zeolites are suitable for cation exchange and, hence, can be used for reducing the Na^+ content.

Therefore, it can be concluded that zeolites, which are available in large amounts at low cost, can be used for ion exchange. In the study conducted by Vance *et al.*, various kinds of natural zeolites were used in the form of filled columns to lower SAR. Clinopetiolite, which enjoys high thermal stability, was one of the zeolites they employed (Vance *et al.*, 2004).

Use of natural zeolites as ion exchange materials has the following advantages:

- Zeolites are found near the earth's surface and are easy to extract
- They are usually available in large amounts, especially in Iran where there are rich resources of these compounds and various types of zeolites are easily found at low prices
- They have high purity (more than 75%)

In this study, the feasibility of using natural zeolites in treating ROC was studied. The purpose was to investigate changes in the SAR parameter in the presence of two kinds of zeolites (clinopetiolite and metacaoline) at various concentrations and consider the effects of presence or absence of EDTA.

MATERIALS AND METHODS

The effects of zeolites (clinopetiolite and metacaoline) at 5, 7, and 10 grams per 50 cc ROC and the presence of EDTA in a 48-hour interval were investigated. Twenty-four laboratory samples were studied and measured. Clinopetiolite was employed in 12 of the sample units and metacaoline in the other 12. Concentrations were adjusted at three levels and EDTA was considered a Bernoulli variable at two levels depending on its presence or absence in the experiment container. Based on this, $3 \times 2 = 6$ sample units were adjusted for each zeolite in two time groups. Re-measurements were made forty-eight hours after the initial measurements to see whether passage of time influenced the values of the response variables in each of the 12 studied units.

In one series of experiments, the zeolite was washed with 1M HCl acid and then with 1M NaOH and several times with distilled water before conducting the zeolite test. This was done to reduce the ion content in the zeolite structure.

The experimental design included three intersecting variables and one repeated measures factor (the time factor) but, due to measurement limitations in the laboratory, the 4- factor design with 4 intersecting factors was employed (Table 1). This table specifies the levels of each factor (the effects are generally stabilized).

Table 1: Experimental design

	Row	Factor	Number of levels	Type of effect	Levels
Intersecting factors	1	Substance (zeolite)	2	Stabilized	Clinopetiolite and metacaoline
	2		3	Stabilized by researcher's choice	5, 7, and 10 gram per unit volume
	3		2	Bernoulli stabilized	Zero and one
	4		2	Stabilized by researcher's choice	Start of experiment (Zero time) and 48 hours later

RESULTS AND DISCUSSION

The 4-factor design was considered with one repetition to analyze the effects of various factors on response variables, and the interaction effect of the third order and higher of the intersecting factors (based on effect hierarchy principle) was omitted to allow mean square errors calculation.

Therefore, the main effects and the interaction effects of the second order in the design model were considered.

ANOVA was performed, with this explanation that one multivariate analysis of variance (MANOVA) (with two variables) was performed instead of two, because of the logical correlation between the response variables, by considering a response vector the components of which were the SAR response variable.

The 4-way MANOVA with Build Term(s): Interaction structure was employed. Test statistics were also calculated based on Wilks' lambda method.

The main effect of a factor refers to increasing or decreasing effect of changes in the response variable with changes in the level of the main factor, and the interaction effect between two factors refers to the above-mentioned changes that happen in one factor in relation to the levels of another factor.

In Table 2, the significance level of the null hypothesis (the p-value) is for conclusions drawn in the hypothesis testing, the null hypothesis of which is "no source effect" and the alternative hypothesis of which is "source effect."

Therefore, rejection of the null hypothesis will make the related effect significant. Since 5% error of the first kind in the experiment was acceptable, if the level of significance of the null hypothesis declined below 0.05, it meant the null hypothesis was rejected at the level of 5% and the related effect was accepted.

As shown in Table 2, none of the main effects or the interaction effects was significant at the 0.05 level. Stated more clearly, there were no differences between the different concentration levels.
Therefore, it can be acknowledged that concentration was not a determining factor (at least in the 5 to 10 gram interval).

Table 2: MANOVA table for the factor model without the interaction of the effects of three factors and more in the first model of the first experiment

Source effect	The statistical value of Wilks' lambda	The F statistic	20 types of degrees of freedom	Degree of freedom for error	The significance level of the null hypothesis
y-intercept	0.002	2501.362	2	8	0.000
Time	0.203	15.719	2	8	0.002
Material	0.323	8.371	2	8	0.011
Concentration	0.710	0.749	4	16	0.573
EDTA	0.046	83.171	2	8	0.000
Time× Material	0.323	8.371	2	8	0.011
Time× Concentration	0.710	0.749	4	16	0.573
Time × *EDTA*	0.193	16.691	2	8	0.001
Material× Concentration	0.781	0.526	4	16	0.718
EDTA× Material	0.557	3.178	2	8	0.096
Concentration× *EDTA*	0.749	0.621	4	16	0.654

On the other hand, the presence of EDTA was significant in increasing the value of the SAR variable. In fact, it had a negative effect on the overall results of the experiment (Table 3). Therefore, not only were the EDTA factor and all its effects omitted from the model in the remaining part of the research but the related treatments were also omitted in the calculations that followed.

Table 3: The separate averages of the different response variables for the various effective factors identified in the first step of analysis in the first experiment

Effective factors			Averages of response variables
Time	Materials	EDTA	SAR
Start	Clinopetiolite	Absent	153.90
		Present	275.00
	Metacaoline	Absent	153.90
		Present	275.00
48 hours	Clinopetiolite	Absent	102.27
		Present	495.57
	Metacaoline	Absent	44.10
		Present	371.23

Table 4 reports the results of analysis in the second step based on the new model with the time and materials factors. The effects of the main factor and the mutual effects of time and materials were significant

Table 4: The MANOVA table in the second step for the factor model of time and materials (the second model) in the first experiment

Source effect	Value of Wilks' lambda statistic	F statistic	Types of degrees of freedom	Degree of freedom for error
y-intercept	0.000	16525.234	2	7
Time	0.020	170.229	2	7
Materials	0.017	203.004	2	7
Time× *Materials*	0.017	203.004	2	7

Conclusion

As was previously mentioned, concentration is not a determining factor (at least in the 5 to 10 grams interval). Therefore, it can be concluded that zeolite concentration may be adjusted and designed at minimum levels in large- scale operations. Based on the results of analysis of this experiment, concentration was an ineffective factor and EDTA an undesirable factor, and its clearly undesirable effects in a series of elementary experiments led to its omission from the project.

Figures 1 and 2 show the diagrams of percentage reduction in SAR caused by using zeolites in different states. According to the figures, metacaoline performed better than clinopetiolite (the maximum SAR reduction of about 72% happened when metacaoline was used without being washed). Therefore, this type of zeolites has a high potential for being used in ROC treatment.

Performance of Clinopetiolite in SAR Reduction

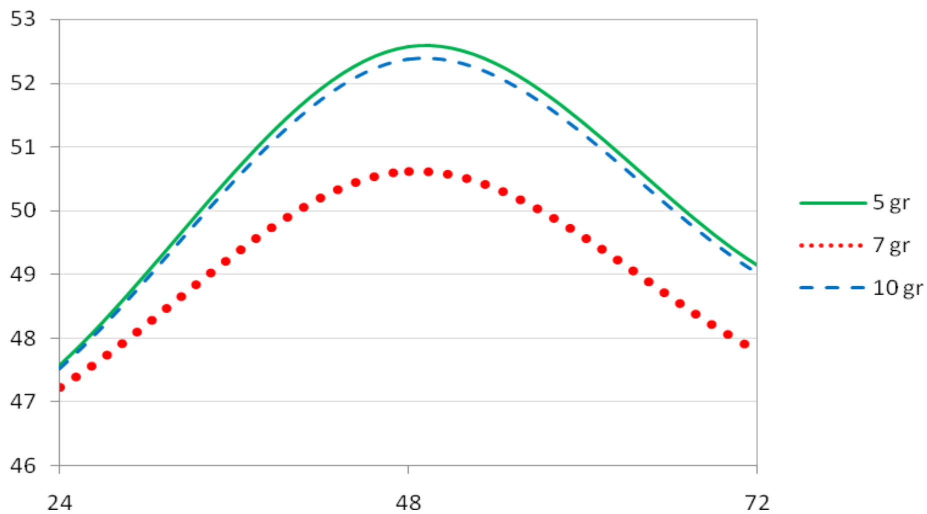

Figure 1: Degrees of SAR reduction in experiments with zeolites

Vertical axis: percentage reduction in SAR; Horizontal axis: time in hours

Performance of Metacaoline in SAR Reduction

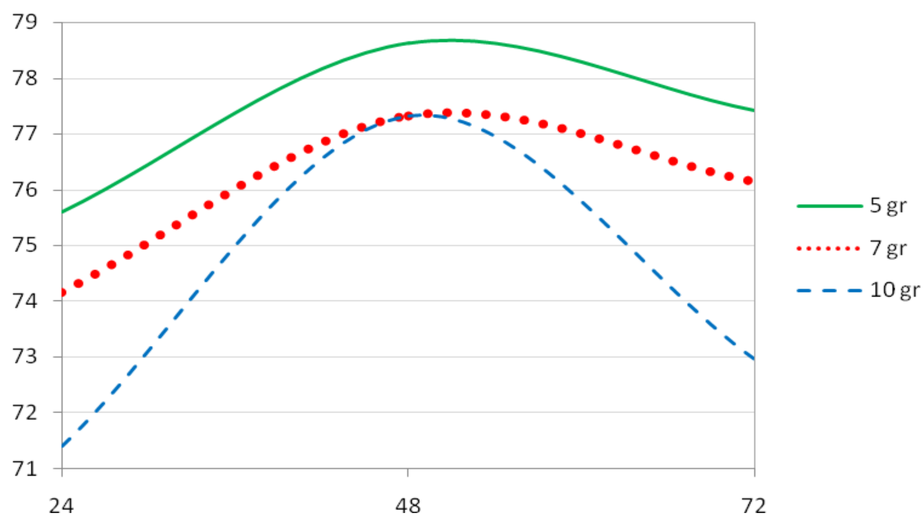

Figure 2: Degrees of SAR reduction in experiments with zeolites

Vertical axis: percentage reduction in SAR; Horizontal axis: time in hours

Of course, it is worth noting that the water fed into the studied reverse osmosis process was taken from a river that was near the unit. Therefore, it lacked the additional microbial or chemical pollution found in urban or industrial wastewater. Consequently, it can be used in agriculture and in irrigation, if treated with zeolites.

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